Harding Lawson Associates

October 1, 1998

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Re: Response to Comments
Phase I Treatability Study Draft Report
Perchlorate in Groundwater
Baldwin Park Operable Unit, San Gabriel Basin

Dear Mr. McGuire:

Attached you will find a copy of our revised report "Draft Final Phase 1 Treatability Study Report, Perchlorate in Groundwater, Baldwin Park Operable Unit, San Gabriel Basin". We believe that this revised report addresses your comments dated June 12, 1998. Comments made by the U.S. Environmental Protection Agency (EPA) and the Baldwin Park Operable Unit Steering Committee's (BPOUSC) responses to these comments are included as Appendices G and H respectively. Our responses to your comments are detailed below. A revised Phase 2 Treatability Study Work Plan will follow under separate cover.

Organic By-Products of GAC/FB Process

1. Only a limited number of organics were monitored for in the reactor effluent. Because a biological process of any kind (and especially one conducted in anoxic conditions) can produce a wide variety of organic compound by-products, it is important to look for a wide variety of organics. Equations on pages 6 and 9 in the text are not correct because they grossly oversimplify the reactions taking place. A lot more material than carbon dioxide and water are produced in the reactor. Not only secular material being produced as a result of using ethanol as a carbon source, but also a wide variety of bacterial metabolic by-products such as aldehydes, ketones and organic acids may be produced. While not mentioned in the text, the data tables in Appendix D show the production of several hundred micrograms per litre of acetone in the reactor effluent. Broad-scan analytical methods for more polar organic compounds should be used to identify the by-products of ethanol degradation and cell metabolism and growth. Derivatization techniques followed by GC/MS and liquid chromatography/mass spectroscopy (LC/MS) should be used to identify these organic compounds and quantify their amounts.

   Response: (i) In Phase 2, the BPOUSC will analyze the effluent for Title 22 parameters using methodologies consistent with regulatory levels. In addition Phase 2 analytical work will include testing for a broad range of organic compounds. Although specific test methods have not yet been selected, input has been gathered from the appropriate parties and the Phase 2 Treatability Study Work Plan will propose specific methods. (ii) The equations in the text represent perchlorate and nitrate reduction neglecting cell synthesis. They are not intended to represent all reactions

occurring in the bioreactor. (iii) Methanol, methyl isobutyl acetone, and isopropyl alcohol were detected as impurities in the ethanol. Although acetone was not detected as an impurity in the ethanol the limit of detection was 0.5 percent. Therefore, concentrations of acetone consistent with bioreactor influent concentrations would not have been detected. Acetone increased across the bioreactor while MIBK decreased. We hypothesis most of this increase was due to breakdown of MIBK. Alternative mechanisms, such as the oxidation of the alcohols, could have a role in the acetone increase; however, with the bioreactor in reducing conditions this is not a favored mechanism. To simplify these issues during the Phase 2 Treatability Study a higher grade of ethanol will be located and used.

2. More volatile organic compounds (VOCs) must be analyzed for in the reactor effluent. It is unlikely that the disappearance VOCs noted in Appendix D means that the compounds were biologically converted to carbon dioxide and water. Results for only a limited number of VOCs are listed in Appendix D. A purge-and-trap isolation methodology followed by GC/MS with compound identification and quantification should be carried out at maximum process efficiency and at sub-maximum process efficiency such as during start up. The investigators may wish to do a preliminary scan with purge-and-trap/GC with an electron capture detector (ECD) to screen for halogenated volatile organic by-products.

   Response: In Phase 2, the BPOUSC will analyze the effluent for Title 22 parameters using methodologies consistent with regulatory levels. In addition purge-and-trap sample extraction followed by GC/MS including compound identification and quantification will be used to scan for a broader range of volatile organic compounds. Details will be provided in the Phase 2 Treatability Study Work Plan.

3. It is most important that an analytical method with a very low (low ppb) method detection level be used to analyze for ethanol (and methanol, for that matter). A level of "less than 5 mg/L" will not be acceptable o the public. The actual level of ethanol must be quantified in the reactor effluent.

   Response: In the Phase 2 study, we will evaluate water quality parameters consistent with the regulatory limits for various constituents detailed in Title 22. Because of concerns regarding the presence of ethanol and methanol in water produced by the treatment plant, analytical methods which achieve the lowest possible detection limit using standard and accepted methods will be used. During Phase 1 the analyses provided in Appendix D were used to evaluate perchlorate reduction in the bioreactor and were not used for a comprehensive constituent analysis as will be performed to ensure potability of produced water.

4. This biological process is undoubtedly producing food that other microorganisms could use in an aerobic environment such as a water utility distribution system. Acetone which is acknowledged to be produced during perchlorate reduction in the GAC/FB reactor will act as a food source. The investigators should have taken samples from the reactor influent and effluent and submitted them for Assimilable Organic Carbon (AOC) or Biodegradable Organic Carbon (BDOC) analysis. These tests have been able to estimate the amount of "food" that the ozonation process can produce when it oxidizes natural organic matter. Also, there is not even any total organic carbon (TOC) data from the study. The reader does not even know if there is a net production of TOC through the process (as compared to the groundwater values). BOD and COD do not even begin to address the issue of organic production in the process. The distribution system downstream of the treatment process could be subject to regrowth of bacteria if a high concentration of food passed into it.

   Response: The Phase 1 study was not intended to evaluate production of organic compounds across the bioreactor. This will be addressed in Phase 2. The Phase 2 study will employ AOC, BDOC, and TOC analyses as suggested. The BOD and COD analyses in Phase 1 were not intended to evaluate the potential for downstream distribution of food for regrowth of bacteria. BOD and COD are typical parameters that are used by wastewater treatment plants and were tested to provide a basis of comparison to other processes. During Phase 2 a comprehensive treatment train which includes unit processes that will remove or destroy total organic carbon will be employed and the influent and produced water will be monitored as recommended.

Disinfection By-Products (DBPs)

1. I was very surprised to note that the critical issue of disinfection by-product production [DBP] was not addressed in the Phase 1 study in even a cursory manner. Given the amount and type of organics present in the reactor effluent (especially as noted by the increase in acetone), it is expected that chlorination of the reactor effluent will produce hundreds of ppb of trihalomethanes and other DBPs. The authors stated that the effluent met all Title 22 parameters, but did not see any THM or other DBP data. Therefore, we do not know if the reactor (followed by chlorination and filtration) can meet drinking water standards or not. This must be addressed before the process can be considered for use in a drinking water distribution system. The work plan for Phase 2 mentions collecting data on DBPs but not much detail is provided. I recommend analyzing for the same DPBs as are monitored for in the Information Collection Rule after the chlorination step that is sufficient to kill the resident bacteria (see discussion below).

   Response: The Phase 1 study was not intended to address DBP production. DBP will be analyzed in a manner consistent with the Information Collection Rule. The effluent was evaluated for primary and secondary water quality parameters on 5/18 and 6/15/98. The text has been modified accordingly. Although this pilot-scale study included the analysis of bioreactor effluent for the range of water quality parameters used to regulate potable water it was not an objective of this

testing to produce potable water. To produce potable water and to fully evaluate the effectiveness of filtration and disinfection technologies, these unit processes must be part of the treatment train. Testing of filtration and disinfection technologies will be performed during a Phase 2 perchlorate treatability study. This study will be designed to meet treatment requirements of the Surface Water Treatment Rule.

Secondary Drinking Water Standards

1. Utilities must not only meet primary drinking water standards but they must also produce water that is aesthetically acceptable to its customers. At no place in the reports is there a discussion of the taste and odor or color characteristics of the water. A Flavor Profile Panel should assess the taste and odor quality of the reactor product water.

   Response: The taste, color, and odor of the produced water will be addressed during the Phase 2 Treatability Study. We agree that these are important water quality characteristics but since the Phase 1 Treatability Study did not include filtration or disinfection unit processes testing of the effluent from the bioreactor for taste, color, and odor would not have produced meaningful results.

Microbiological Quality of the Reactor Effluent

1. The report deals in only passing fashion with the issue of microbiological quality of the reactor effluent. There is an error on page 13 where an "upper quantifiable limit" for coliforms is stated to be 200.5. In fact, much higher concentrations of coliforms can be determined if the dilutions tested are properly planned. Also, there are limited total plate count bacteria levels (or at least that is what they appear to be) in Appendix D. They are not discussed in the text. All of the data indicate that a significant and potentially troublesome of level of bacteria are shed by the reactor and end up in the reactor effluent.

   Response: No attempt was made to quantify MPN > 200.5. Quantification for MPN > 200.5/100 mL requires dilution of the sample or that the Quantitray method be used. Unfortunately provisions were not made with the laboratory to dilute samples or perform the Quanitray method at the time the samples were submitted for analysis. Testing of water produced following filtration and disinfection unit processes will be performed during the Phase 2 study.

2. The report assumes that disinfection with chlorine and filtration will fix the biological problem, but they do not discuss any of the treatment process integration or confounding issues. For example, it may be necessary to operate the filter in a "biologically active" mode to remove the organics created by the GAC/FB reactor. If so, chlorination must follow the filter and not precede it as noted in the experimental for Phase 2. Also, adding chlorinate at the level to kill the bacteria could cause production of very high levels of DBPs given the production of precursors I referred to above.

   Response: As discussed above, the text has been modified to reflect that further testing needs to be completed on disinfection and filtration of the effluent. Although a more complete description of the proposed treatment train for the Phase 2 Treatability Study will be provided in the Work Plan, modification to this treatment train have been made to address these concerns. The bioreactor will be followed by a biologically active multimedia filter. Disinfection will follow all other unit processes.

3. Chlorination after the filter is also a good idea because the clumps of bacteria will likely be removed in the filter. Clumping of bacteria has been demonstrated by many researchers to impede the action of disinfectants like chlorine. The bacteria in the center of the clump can be protected by the bodies of the surrounding bacteria. It is important to remove or kill the majority of bacteria before the water is put into a distribution system to avoid "seeding" the system with coliforms or other nuisance organisms.

   Response: Agreed. See response (2). Filtration is the unit process that will immediately will follow the bioreactor as suggested.

Parameter Selection of Data Presentation

1. Measuring BOD and COD as parameters for understanding the process is not advisable. Total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV254) are much more relevant to drinking water treatment.

   Response: BOD and COD are typical parameters that are used by wastewater treatment plants and were tested to provide a comparison to other processes. Parameters used to monitor operational performance will be more fully developed in Phase 2. This will include analysis for TOC. In addition the proposed treatment train for the Phase 2 Treatability Study will include ultraviolet light to remove N-nitrosodimethylamine (NDMA) and therefore ultraviolet absorbance at 254 nm (UV254) will be addressed.

2. It would be easier for the reader to assess the importance of elevated perchlorate levels in the reactor effluent on Plate 3 if the y-axis began at zero as it does for all the other graphs. Also, the method detection level (MDL) should be noted on the various graphs to put the "plateauing" or "steady-state" effect on the graphs in perspective.

Response: A quantitation limit for perchlorate has been added to the appropriate figures. Although the axis on Plate 3 was not fixed in the Draft Final report we will fix it to show a y-axis that starts at zero in the Final Report.

Reactor Response after Process Upset

1. The report clearly documents that the biological reactor is subject to upset during power outages or interruptions in the chemical feeds. Recovery times were on the order of days. Unit processes used in water treatment must be reliable a very high percentage of the time or backup systems must be in place to deal with process upsets. There is no discussion of this in the report which I believe is a major weakness and should be corrected. If backup systems will have to be included in a full-scale system, that will adversely affect the economics of the treatment process.

   Response: Please see Section 5.4.6 "Bioreactor Response and Biomass Stability." There are three conditions under which bioreactor stability was evaluated; planned shutdowns, unplanned shutdown, and flow ramp up. Under planned shutdowns, bioreactor circulation was maintained and system recovery was rapid (approximately 24 hours) but analyses at less than 24 hour increments were not performed. During unplanned shutdowns, no bioreactor circulation was maintained. Although system recovery occurred within two days, samples were not collected at a more frequent interval. Therefore, the system could have recovered significantly faster. During flow ramp up when the biomass was healthy, the bioreactor typically responded within 24 hours. Our conclusion is that bioreactor response is rapid as long as the maximum design rate is not exceeded. This is the expected planning case. Other types of bioreactor upset would only occur in rare circumstances where the biomass is poisoned by a toxin, an unlikely event when using a groundwater supply.

Summary

1. I do not believe the study has demonstrated that filtration and disinfection that the water produced by the treatment train will meet "potable standards". A number of parameters included in Title 22 were not analyzed and no assessment of DBP formation was performed. Also, no assessment of the secondary maximum contaminant levels has been done. Consumers will reject the water produced by the reactor if it is colored, has a bad odor or an off-taste. The authors can only speculate on compliance with Title 22 since they have not done the work.

   Response: The report has been modified accordingly: "The study demonstrated that water produced from the intended treatment train will potentially meet State and Federal potable water standards. Additional work is needed to evaluate disinfection and filtration and demonstrate that the treatment processes will reliably produce potable water." Responses to previous comments

address the issues related to testing which will be performed during the Phase 2 Treatability Study. These issues include the removal of biological material prior to disinfection, the identification and quantification of disinfection by-products, analyses for other organic compounds by GC/MS, analysis for ethanol impurities and possible bioreactor by-products using methods with lower detection limits, and analysis for color, odor, and taste.

Recommendation

1. Before Aerojet and La Puente Water District go to the expense of a demonstration-scale test of technology, I recommend that the pilot plant in Sacramento be restarted and additional analyses be conducted (see above discussion topics). I believe more work should be done to see if the possibly serious problems with disinfection by-product formation could be resolved before the demonstration-scale project is built. If the organic products from the reactor are significant precursors for the formation of disinfection by-products, the entire process may not be viable.

   Should the DBP tests prove to be satisfactory, I recommend that an alternate arrangement of unit processes be considered. Figure 1 below shows the filtration process following immediately after the biological reactor with chlorination (or disinfection) following after that and preceding the air stripper. This arrangement will allow further removal of organics on a biologically active filter (an oxygen source may have to be added prior to filtration). In addition, the majority of the particles will be removed prior to chlorination which should improve the chlorination process significantly (lower dose, less contact time to get equivalent kill).

   Response: The Phase 1 treatment system was not designed to include filtration or disinfection, and unfortunately the Phase 1 Treatability Study has been concluded. Phase 2 will include these unit process. The Phase 2 Treatability Study will treat groundwater extracted directly from the San Gabriel Basin. Groundwater tested during the Phase 1 Treatability Study contained concentrations of nitrate and perchlorate similar to that expected in San Gabriel Basin, but was different with respect to other water quality parameters.

   The proposed design for the Phase 2 Treatability Study has been revised both to address your comments and to address the presence of additional chemicals in groundwater at the La Puente Valley County Water District facility. Modifications include placement of a multimedia filter after the bioreactor. This filter will be operated in a biologically active mode. Treatment by uv/oxidation will be added to remove NDMA and 1,4 dioxane. Disinfection will follow all other unit processes.

Thank you for the opportunity to respond to your comments. Perhaps next week we can have a discussion on our proposed treatment train for the Phase 2 Treatability Study and details of the study so that we may properly address your comments before we issue the next draft of this work plan.

Yours very truly,

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